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DIE ATTACH ADHESIVES WITH EPOXY RESIN
HAVING ALLYL OR VINYL GROUPS

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This invention relates to die attach adhesives with improved adhesion
10 due to the presence of epoxy resin with allyl or vinyl unsaturation.

Adhesive compositions are used for a variety of purposes in the
fabrication and assembly of semiconductor packages, such as, the bonding
of integrated circuit chips to leadframes or other substrates, and the bonding
of circuit packages or assemblies to printed wire boards. Major requirements
15 for these uses are fast cure and high adhesive strength, traditionally achieved
with epoxy resins. Epoxy resins, however, can be brittle, and other resins
have been evaluated and employed to bring flexibility, hydrophobicity, and
other properties to die attach adhesives. The alternate resins, in turn, do not
always display the strong adhesion provided by the epoxy resins. Therefore,
20 there is a need for die attach adhesives that incorporate a balance of
properties to meet all the requirements for an adhesive used in the
manufacture of a semiconductor package.

This invention is an adhesive composition comprising (a) a resin
capable of cure by free-radical polymerization, that is, having carbon to
25 carbon unsaturation, or capable of cure by hydrosilation, that is, having
silicon-hydride groups, (b) an epoxy compound that contains allyl or vinyl
unsaturation, (c) a curing agent for the resin and a curing agent for the epoxy,
and (d) optionally, one or more fillers. The composition may also contain

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adhesion promoters or coupling agents. The inventors discovered that the addition of the epoxy compound containing allyl or vinyl unsaturation gave an
5 unexpected increase in adhesion performance to the base resin containing the carbon to carbon unsaturation. In another embodiment, this invention is a semiconductor package having a semiconductor die adhered to a substrate with the inventive adhesive.

Free-radical curable resins, which can be used as adhesives in
10 microelectronic applications, include, for example, maleimides, such as those available from Ciba Specialty Chemicals; siloxanes and polysiloxanes, such as those available from from Gelest; polyethers, such as those available from from BASF; polyesters, such as those available from from Uniqema or Bayer; poly(butadiene)s, such as those available from from Elf-Atochem;
15 polyurethanes, such as those available from from Bayer or BASF; and acrylate resins, such as those available from from Sartomer or UCB Radcure. Siloxanes and polysiloxanes, which cure by hydrosilation, may be linear or cyclic polymers, and will have at least 2 silicone-hydride functionalities per molecule. The polyethers, polyesters, and polyurethanes preferably will
20 contain terminal unsaturation, but may also contain unsaturation within the polymer chain. The particular resin will be chosen by the practitioner to give specific material properties in a final formulation, such as, rheological properties, hydrophilic or hydrophobic properties, toughness, strength, or flexibility. The resin will be present in the adhesive composition in a range of
25 10-80% by weight.

The epoxy compounds may be any epoxy compounds with allyl or vinyl functionality. Examples include 2,6-diglycidylphenyl allyl ether, limonene dioxide, glycidyl vinyl benzyl ether or glycidyl vinyl ether. The



epoxy will be present in the adhesive composition in a range of 0.1-30% by weight.

Exemplary curing agents for the base resins are free-radical initiators, which can be thermal- or photo-initiators. The initiators will be present in the adhesive composition in an amount of 0.1% to 10%, preferably 0.1% to 3.0%, by weight. Preferred thermal initiators include peroxides, such as butyl peroctoates and dicumyl peroxide, and azo compounds, such as 2,2'-azobis(2-methyl-propanenitrile) and 2,2'-azobis(2-methyl-butanenitrile). A preferred series of photoinitiator is one sold under the trademark Irgacure by Ciba Specialty Chemicals. In some formulations, both photo-cure and thermal cure may be desirable, for example, the curing process can be started by irradiation, and in a later processing step curing can be completed by the application of heat.

Exemplary curing agents for the epoxy functionality on the epoxy resin are Lewis bases, for example, amines, such as Ancamine 2337xs, and 4,4'-bis(para amino cyclohexyl) methane, both commercially available from Air Products; imidazoles, such as Curezol 2E4MZ-CN, a product of Shikoku Chemicals; amides, such as, Dicyanamide, a product of Air Products; polyamides, such as Versamide 140, a product of Henkel; tertiary amines, such as Amicure DBU, a product of Air Products. Alternatively, Lewis acids, such as Rhodorsil 2074 [(tolylcumyl) iodonium tetrakis (pentafluorophenyl) borate], a product of Rhodia, or GE UV9380C, a product of General Electric, can be used to initiate a cationic cure. The curing agent for the epoxy functionality will be present in the composition in a range of 0.1 to 3 % by weight of the total formulation.

In general, these compositions will cure within a temperature range of 70°C to 250°C, and curing will be effected within a range of ten seconds to three hours. The time and temperature curing profile of each formulation will



vary with the components of the formulation, but the parameters of a curing profile can be adjusted by a practitioner skilled in the art without undue experimentation.

5 In some compositions it may be desirable to add organic or inorganic fillers. Suitable conductive fillers are carbon black, graphite, gold, silver, copper, platinum, palladium, nickel, aluminum, silicon carbide, boron nitride, diamond, and alumina. Suitable nonconductive fillers are particles of vermiculite, mica, wollastonite, calcium carbonate, titania, sand, glass, fused
10 silica, fumed silica, barium sulfate, and halogenated ethylene polymers, such as tetrafluoroethylene, trifluoroethylene, vinylidene fluoride, vinyl fluoride, vinylidene chloride, and vinyl chloride. Although optional, when present, fillers will be in amounts of 20% to 90% by weight of the composition.

 Suitable adhesion promoters or coupling agents are silanes, silicate
15 esters, metal acrylates or methacrylates, titanates, and compounds containing a chelating ligand, such as phosphine, mercaptan, and acetoacetate. When present, coupling agents will be in amounts up to 10% by weight, and preferably in amounts of 0.1% to 3.0% percent by weight.

 The invention is further illustrated by the following examples, which
20 are not intended as a limitation on the invention.

 Semiconductor packages, consisting of a silicon die adhered to a bond pad on a leadframe with an adhesive, the die and the leadframe encapsulated in a molding compound, are tested for reliability using a test protocol of JEDEC Solid State Technology Association identified as JESD22-
25 A112. In this method, the semiconductor package is subjected to 85°C and 85% relative humidity for 168 hours followed by exposure to 240°C in an infrared oven using a standard solder reflow ramped profile of five minutes.



Reliability failure of the package manifests itself as delamination of any of the package interfaces or as cracked molding compound.

Previous experiments of the inventors testing for failure of the adhesive adhering the die to the leadframe were conducted using
5 unencapsulated assemblies of a die adhered to a leadframe with die attach adhesives. In these experiments, the unencapsulated assemblies were cured in an oven at 175°C for 30 minutes. After cure, the assemblies were divided into two groups. The first group was tested for die shear strength after exposure to a hot dry environment, which consisted of 240°C for one
10 minute, followed by 175°C for four hours.

The second group was tested for die shear strength after exposure to a hot wet environment, which consisted of 85% relative humidity at 85°C for 168 hours.

After exposure, each group of assemblies was heated to 250°C, after
15 which the die was sheared from its substrate. Some of the assemblies exhibited cohesive mode failure of the adhesive adhering the die to the leadframe, others exhibited adhesive mode failure of the adhesive adhering the die to the leadframe.

Those adhesives that failed in a cohesive mode correlated with
20 higher reliability in the JEDEC test method on encapsulated packages using the same adhesive, while the adhesives that failed in the adhesive mode giving a clean metal surface, correlated with lower reliability in the JEDEC test method on encapsulated packages using the same adhesive.

In the following examples, formulations with and without the epoxy
25 with allyl or vinyl functionality were tested for hot dry die shear strength (measured in kg of force), and for hot wet die shear strength using the above described protocols. The die used was a silicon die, 12.5mm x 12.5mm x 0.38mm adhered to a bare copper or a silver-plated leadframe.

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The adhesive composition and performance test data are set out in the following tables and show that the adhesive formulations containing epoxy with allyl or vinyl functionality failed during hot wet die shear testing in a cohesive mode, while the formulations without the epoxy containing allyl or vinyl functionality failed in an adhesive mode. Therefore, the data indicate that the formulations containing the epoxy compound with vinyl or allyl unsaturation improve adhesive performance and semiconductor package reliability. The compositions are reported in weight percent.

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EXAMPLE 1

COMPOSITION Ex.1	With epoxy resin with allyl functionality		With epoxy resin without allyl functionality	
proprietary bismaleimide	19.04%		19.04%	
4,4'-bismaleimido-diphenylmethane	0.52%		0.52%	
(2,6-diglycidylphenyl allyl ether) epoxy resin	1.2%		---	
bis-phenol-F epoxy resin	----		1.57%	
poly(budadiene) (Ricon 130)	2.61%		2.61%	
polyester vinyl ether resin (Allied signal VE1312)	1.57%		1.57%	
adduct of cinnamyl alcohol with dimer diisocyanate	3.39%		3.39%	
methacryloxy silane (Witco A-174)	0.4%		0.4%	
1,1-di(t-amyl peroxy) cyclohexane (Witco USP90MD)	0.65%		0.65%	
2-ethyl 4-methyl imidazole-CN	0.25%		0.25%	
silver flake	70%		70%	
Total	100%		100%	
PERFORMANCE Ex.1	Silver-plated leadframe	Bare Copper leadframe	Silver-plated leadframe	Bare Copper leadframe
Cured for 30 minutes/175°C Die warpage @ RT	15.5μ	8.3μ	18.6μ	7.1μ
Hot Dry Die Shear @ 250C	14.1kg cohesive	12.3kg cohesive	1.3 kg adhesive	1.8 kg adhesive
Hot Wet Die Shear @ 250C	7.3 kg cohesive	6.24 kg cohesive	1.3 kg adhesive	1.6 kg adhesive



EXAMPLE 2

COMPOSITION EX.2	With epoxy resin with allyl functionality		With epoxy resin without allyl functionality	
polybutadiene with acrylate functionality (Ricon, 1756)	10.5%		10.5%	
polybutadiene with maleic anhydride functionality (Ricon, 130MA10)	2.0%		2.0%	
1,6-diol diacrylate (Sartomer SR238)	2.0%		2.0%	
isobornyl acrylate (Sartomer SR506)	5.0%		5.0%	
1,1-di(t-amyl peroxy) cyclohexane (Witco USP, 90MD)	0.5%		0.5%	
lauryl acrylate (Sartomer SR335)	2.5%		2.5%	
2,6-diglycidylphenyl allyl ether	2.0%		0%	
2-ethyl 4-methyl imidazole-CN	0.2%		0%	
silver flake	75%		75%	
Total	100%		100%	
PERFORMANCE Ex.2	Silver-plated leadframe	Bare Copper leadframe	Silver-plated leadframe	Bare Copper leadframe
Die Warpage at room temp. Cured for 30 minutes/175°C Plus 1 minute/220°C or Plus 4 hours/174°C *delaminated		22.5μ 26.6μ 19.7μ		17.0μ 17.5 μ 12.1 μ
Hot Dry Die Shear @ 250C failure mode		6.6kg cohesive		1.3kg adhesive
Hot Wet Die Shear @ 250C failure mode		2.8kg cohesive		1kg adhesive

Note:

- 5 Adhesion to Ag-plated leadframe was satisfactory for both formulations.



EXAMPLE 3

COMPOSITION Ex.3	With epoxy resin with allyl functionality	With epoxy resin without allyl functionality
Sycar resin *	13.96	11.56
Polybutadiene (Ricon Resins, Ricon 130)	2.33	1.93
Poly(butadiene) functionalized with maleic anhydride (Ricon Resins, Ricon 130/MA8)	1.4	1.16
Poly(butadiene) functionalized with maleic anhydride (Ricon Resins, Ricon 130/MA 20)	0.23	0.20
Diallyl bisphenol-A (Bi-Max)	1.63	1.35
Divinyl ether (ISP Tech, DVE-3)	1.16	0.96
(2,6-diglycidylphenyl allyl ether) epoxy	----	2.90
1,3-bis (glycidoxypentyl) – tetramethyldisiloxane (Gelest, SIB 1115.0)	----	0.58
Rhodorsil 2074 (Rhone Poulenc)	----	0.6
fumed silica (Degussa, 812S)	0.5	0.5
silver powder (Chemet, K-0082P)	78	78
platinum complex* (Sivento Inc., CPC 085)	0.4	0.4
platinum complex* (Sivento Inc. CPS 925-P)	0.4	0.4
Total	100%	100%
PERFORMANCE Ex. 3**		
Die Shear Strength @200°C, 360x360 mil Si die on PBGA after 48hrs at 85/85	17.0 ± 1.5	15.3±3.2
Failure mode	Adhesive to die backside	Peel off 80% solder mask

*The stock solution as received was diluted with cyclic methylvinylsiloxanes

5 to achieve ~5000ppm Pt concentration.

** The adhesive compositions were dispensed on a metal lead frame and cured in a convection oven by ramping from room temperature to 175C over 30 minutes then holding at 175C for 15 minutes.

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CLAIMS:

1. A die attach adhesive composition comprising:
 - (a) a resin capable of curing by free-radical polymerization or by
5 hydrosilation, present in an amount of 10% to 80% by weight,
 - (b) an epoxy compound having vinyl or allyl functionality, present in
an amount of 0.1% to 30% by weight,
 - (c) a curing agent for the epoxy compound, present in an amount of
0.1% to 3% by weight,
 - 10 (d) a curing agent for the resin, present in an amount of 0.1% to 10%
by weight, and
 - (e) optionally, a filler, present in an amount of 20% to 90% by weight.
2. The die attach adhesive according to claim 1 in which the resin is
15 selected from the group consisting of maleimides, polyethers, polyesters,
poly(butadiene)s, polyurethanes, acrylates, siloxanes, and polysiloxanes.
3. The die attach adhesive according to claim 1 in which the epoxy
compound is selected from the group consisting of 2,6-diglycidylphenyl allyl
20 ether, limonene dioxide, glycidyl vinyl benzyl ether, and glycidyl vinyl ether.
4. The die attach adhesive according to claim 1 in which the filler is
present and is selected from the group consisting of carbon black, graphite,
gold, silver, copper, platinum, palladium, nickel, aluminum, silicon carbide,
25 boron nitride, diamond, alumina, vermiculite, mica, wollastonite, calcium
carbonate, titania, sand, glass, fused silica, fumed silica, barium sulfate,
tetrafluoroethylene, trifluoroethylene, vinylidene fluoride, vinyl fluoride,
vinylidene chloride, and vinyl chloride.